

**CHROMIUM, A DIMER IN SILICATE MELTS?: NEW ELECTROCHEMICAL EVIDENCE ADDRESSING DIMERIZATION AND THE CONDITIONS UNDER WHICH IT IS IMPORTANT.** R. O. Colson<sup>1</sup> and M. C. Colson<sup>2</sup>, <sup>1</sup>Moorhead State University, Moorhead, MN 56563, colson@mhd1.moorhead.msus.edu, <sup>2</sup>Moorhead Junior High, Moorhead MN 56560.

Activities of components in silicate melts are complex functions of the temperature, pressure, and composition of those melts. Variations in activities affect the character of many processes of interest in understanding the petrologic history of the Moon and other planets, including elemental partitioning and phase equilibria. Modeling and prediction of variations of activities in silicate melts are made particularly difficult by our limited knowledge of the actual melt species in which various elements are found. Often melt components are modeled as simplified elemental oxides, even though in many cases these oxides are poor models of the actual speciation in the melt. Electrochemical measurements can provide insight into the thermochemistry of the actual species in the melt, in some cases differentiating the separate effects of the cation and anion in an elemental oxide component [1] or identifying the presence of dimers in the melt [2, 3]. Improvements in our understanding of the nature of the melt species in turn improves our ability to model and understand variations in activity with temperature, pressure, and composition.

Curves for voltammetric reduction of trivalent Chromium to divalent Chromium in silicate melts do not have the shape expected for simple reduction of  $\text{Cr}^{3+}$  to  $\text{Cr}^{2+}$  (reported in [3] and seen again in these experiments). The unexpected shape has been interpreted as either the result of coincident reduction of  $\text{Cr}^{2+}$  to Chromium metal [2] or as the result of the presence of a dimer of  $\text{Cr}^{3+}$  (e.g. of the form  $\text{Cr}_2^{6+}$ ) [3]. The primary argument favoring the interpretation of the presence of a dimer is based on the shift in the voltammetric peak position with changing Cr concentration, as expected if a dimer is present [4]. However, the experimental results we report in Fig. 1 illustrate that the shift in peak position with concentration disappears at lower concentrations of Cr and possibly at higher temperatures. This suggests either that it is not a dimer causing the unusual voltammetric curve shape, or that the effect of the dimer changes with changing temperature and concentration.

**Are there Cr dimers in the melt?** The alternative interpretation of the results in Fig. 1 is that the odd shape of the voltammetric curves is due to coincident reduction of divalent Cr to a metal dissolved in the Pt electrodes used in these electrochemical experiments. Solution of reduction products in Pt electrodes during cyclic voltammetry has been reported previously [2, 5]. At sufficiently high Cr concentrations in the melt, and sufficiently high voltammetric scan rates, the concentration of the Cr in the Pt during reduction could ex-

ceed the concentration limits for Henry's Law behavior. This would result in a shift in the cyclic voltammetric peak position as concentration in the melt changes. The expected direction of the shift would be the same as that observed in these experiments. This shift in peak position would cease to occur once the concentration fell low enough so that Henry's Law behavior in the Pt electrode is preserved, thus possibly explaining the results seen in Fig. 1. This type of behavior has been reported for electrochemical reduction of Fe [2].

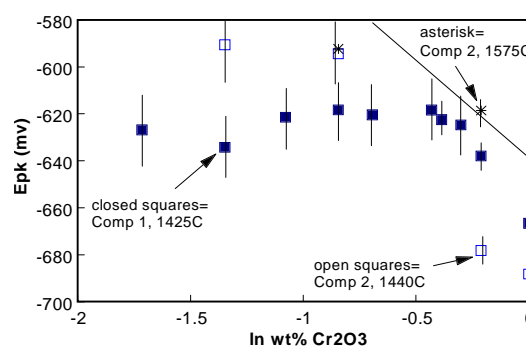


Fig. 1. Cathodic peak position as a function of amount of Cr in 2 different compositions. Composition 1 is  $\text{CaO} \cdot \text{MgO} \cdot 2\text{SiO}_2$ , composition 2 is  $\text{CaO} \cdot \text{MgO} \cdot 1.4\text{SiO}_2$ . The line illustrates the trend expected for dimerization at 1575C from [4]. The trends at 1425C and 1440C are only slightly different. Epk = the potential at the peak cathodic current in a cyclic voltammetry scan. Uncertainties include that due to uncertainties in the measured peak position (about 5-10 mV) as well as possible systematic errors arising from errors in measurement of the electrode surface area (the remainder of the uncertainty). Uncertainties in the measured peak positions are less than those we have previously reported due to use in the present experiments of a SAS fitting procedure to determine peak positions.

However, if the shift in peak position observed in Fig. 1 is related to variations with concentration in the activity coefficient for Cr in the Pt electrode, then the peak position should be a function of experimental current density (or peak current). The current density increases both with the initial concentration of Cr in the melt and the voltammetric scan rate. Figure 2 illustrates that there is little correlation between the shift in peak position and the current density, indicating that non-Henry's Law behavior of Cr in Pt is not likely the cause of the peak shift seen in Fig. 1.

On the other hand, if the shift in peak potential arises from presence of a dimer in the melt, the peak potential should be a function only of initial concentration of Cr in the melt but not scan rate. Fig. 3 illus-



trates that  $E_{pk}$  is closely correlated to concentration, suggesting that a dimer-monomer pair in the melt and not variations in Cr activity in the Pt electrode cause the shift in peak position with concentration.

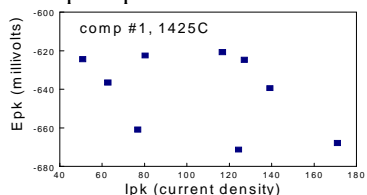


Fig. 2 Lack of correlation between Cathodic peak position and the  $I_{pk}$  suggests that the shift in peak position is not due to changes in the Cr activity coefficient in Pt.

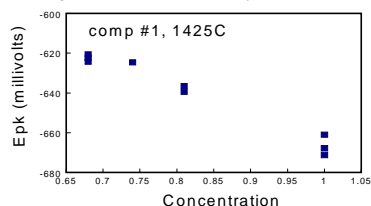


Fig 3. Strong correlation between concentration and cathodic peak position is consistent with a dimer involved in the reduction of  $Cr^{3+}$ . Variation between different scan rates shown for each concentration is within uncertainty.

If a dimer of trivalent Cr is present, why does the peak potential stop shifting when Cr concentrations become sufficiently low? We expect that as concentration decreases, the proportion of trivalent Cr present as a dimer decreases as well ( $K_{eq} = [Cr^{3+}]^2/[Cr_2^{6+}]$ ). At sufficiently low concentration, virtually all trivalent Cr will be present as a monomer and little dimer will be present. Under these conditions, we expect the peak potential will become constant. CVSIM, a program that simulates voltammetric curves for a variety of input conditions [6], illustrates this effect (similar to that observed in Fig. 1). There is an initial increase in the cathodic peak potential which levels off at a peak potential near that expected if no dimer were present (related to the reduction potential for trivalent Cr monomer) (Fig. 4). We can understand this in the following terms: Where substantial dimer is present, the activity of the monomer is greatly decreased from that expected if all Cr were present as monomer, and thus a more negative potential is required to reduce it. As the amount of the dimer decreases, the activity approaches that expected if all Cr were present as a monomer and the trivalent Cr is correspondingly easier to reduce. Once the trivalent Cr is substantially all present as a monomer, additional decreases in Cr concentration, and thus in the proportion of the Cr present as a dimer, has little effect on the activity for the Cr monomer relative to total Cr concentration. The reactions modeled by CVSIM were the following:

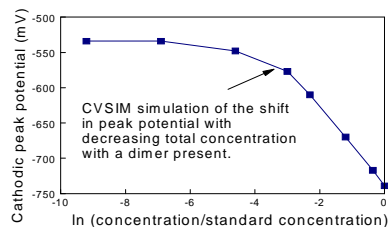
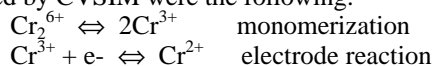


Fig. 4. Simulation using CVSIM [6],  $T=1698K$ .

**Effects of melt composition and temperature on the Cr dimer:** Composition of the melt has an effect on the position of the cathodic peak at any given concentration (Fig. 1). This shift is related to the combined effects of changes in the activity of the oxide ion in the melt (which affects the reference electrode potential) and the stability of the trivalent dimer relative to the monomer in the melt. For the two compositions reported in Fig. 1, the effects of changes in the oxide ion are known [7, 1]. Oxide ion activity variations shift the peak for composition 2 about 90mV in a positive direction. The observed shift is about 20mV in a negative direction, indicating a 110mV shift due to changes in the relative stabilities of the dimer and monomer in the melt. The direction of this shift indicates that the dimer becomes more stable in the more silica-poor composition 2. If this is true, we expect that the dimer will cease to effect the cathodic peak position at a higher total Cr concentration in composition 1 than in 2, an effect seen in Fig. 1. We might expect that higher  $T$  would favor the monomer over the dimer. This is weakly suggested by the shallower slope for the change in peak position with concentration for composition 2 at 1575C than at 1440C, suggesting the high-temperature curve is flattening out at a higher Cr concentration.

**Conclusions:** Additional experiments and evaluations confirm that a dimer of trivalent Cr is present under some conditions in silicate melts. These results suggest that, at least in the simplified melts studied here and at temperatures above 1425C, the dimer is important only at concentrations of  $Cr_2O_3$  near 0.2wt% and greater. The stability of the dimer is a function of composition and in these experiments was more stable in the more  $SiO_2$ -poor composition. The dimer also appears to be more stable at lower temperatures, suggesting that, at lower temperatures, it could be important at concentrations more typical of natural magmas.

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**References:** [1] Colson et al 1995, GCA 59, 909-925 [2] Colson et al 1990, GCA 54, 3353-3367 [3] Colson and Colson, 1995 LPS XXVI, 269-270 [4] Shuman, 1970 Anal Chem 42 521-523 [5] Colson et al 1991 GCA 55, 2831-2838 [6] Gosser 1993, Cyclic Voltammetry Simulation and Analysis of Reaction Mechanisms, VCH [7] Semkow and Haskin, GCA 49 1897-1908.